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Hyperfine-resolved spectrum of the molecular dication DCl^{2+}

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We have obtained hyperfine-resolved infrared spectra of a $^{P}Q_{23}(N)$ branch line in the $v=2$-1 band of the $X\ ^3\Sigma^-$ state of the molecular dication $D^{35}Cl^{2+}$. Analysis of the hyperfine structure allows us to estimate the magnitude of the Fermi contact interaction for the chlorine nucleus; $b_F(\mathrm{Cl})=167$ (25) MHz.

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Introduction. Molecular dications are of interest as minority constituents in laboratory plasmas, astrophysical environments, and the ionosphere [1]. The calculation of dication properties has proven to be far more demanding than molecular structure calculations for similar neutral species [2,3]. The characteristic feature of dication potential-energy curves that have ''volcanic ground states'' [4] is that the molecules are thermodynamically unstable: the long-range part of the potential corresponds to Coulomb repulsion, and only at short range does the potential have a minimum. As shown in Fig. 1, even the minimum of the well is above the asymptote, and all vibration-rotation levels are quasibound. The lifetimes of the resonant levels can vary between years (at the bottom of the well) to one of the order of a vibrational period at, or above, the top of the potential barrier. Thermodynamically stable molecular dications also exist [5], but are not of interest here.

The only molecular dications for which rotationally resolved spectra are known are N_2^{2+} [6], NO^{2+} [7], and DCl^{2+} [8]. The spectra of N_2^{2+} and NO^{2+} were first obtained in emission from discharges; many spectra of N_2^{2+} were subsequently obtained with fast-ion beam techniques [2]. Such measurements were reviewed by Larsson [9]. Abusen *et al.* [8] recently reported a rotationally resolved infrared spectrum of DCl^{2+}, which was obtained using our fast-ion beam/laser beam spectrometer. The deuterium isotopomer was chosen because the calculated vibrational spacings were suitable for interrogation with the CO_2 laser that was available. The preliminary measurements indicate that the spectrum is almost certainly the $v=2\leftarrow1$ band of DCl^{2+} in its $X\ ^3\Sigma^-$ ground electronic state. We now report the observation of well-resolved hyperfine structures in an observed transition.

The hyperfine-resolved measurements of DCl^{2+} represent the most detailed information on the structure of molecular dications that has yet been obtained. A comparison of the measured values of the hyperfine constants with values calculated from first principles shows satisfactory agreement.

Theory. The determination of molecular constants is the experimental measurement of the expectation values of particular operators. The magnetic hyperfine constants (b and c) of importance in molecules were formally defined by Frosch and Foley [10], but we use a slightly different parametrization that has a more simple physical interpretation [11]: $H_{\mathrm{hyp}}=b_F\mathbf{I}\cdot\mathbf{S}+c(3I_zS_z-\mathbf{I}\cdot\mathbf{S})/3+eq_0Q(3I_z^2-\mathbf{I}^2)/4I(2I-1)$, where b_F $(=b+c/3)$ gives the magnitude of the Fermi contact interaction, c determines the magnitude of the axial component of the dipole-dipole term, and eq_0Q determines the magnitude of the nuclear electric quadrupole interaction. Some authors use other symbols: $\alpha(=b+c/3)$, β $(=c/3)$ [12], and $t(=c/3)$ [13].

For a $^3\Sigma^-$ state at the resolution that we can achieve, only these three hyperfine constants are expected to be of importance. For DCl^{2+}, each nucleus has a spin and a quadrupole moment, and there are six hyperfine constants that we might determine. so far we have only been able to resolve hyperfine structure arising from the chlorine nucleus.

The Fermi contact (isotropic-hyperfine) coupling constant b_F, for DCl^{2+}, was determined by calculating the electronic spin density at the chlorine nucleus using unrestricted Hartree-Fock methods. The Fermi contact analysis was carried out using the electron density calculated with a spin-unrestricted quadratic configuration interaction (UQCISD) [14] wave function and Dunning's cc-pV5Z basis set [15]. To provide an improved description of electron density in the region of the nucleus, core/core and core/valence correlation

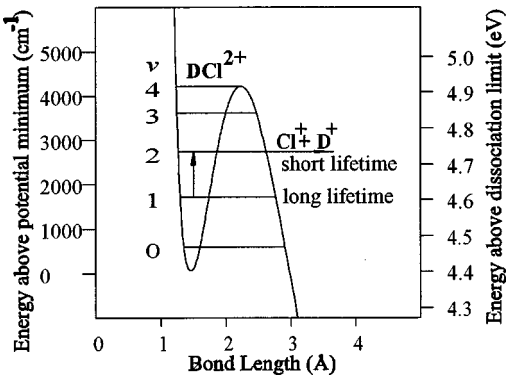

FIG. 1. A potential-energy curve for DCl^{2+} illustrating the principle of the experimental measurements. At resonance, ions are transferred from a long-lived state to a short-lived state and an increase in Cl^+ and D^+ fragments may be observed.

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effects were taken into account by including all electrons in the configuration interaction; to provide a meaningful core/core configuration interaction, core-correlation functions were appended to the initial basis set [16]. As the UQCISD wave function is not an eigenfunction of the spin operator, care was taken to monitor the degree of spin contamination from higher spin states. The electronic structure calculations were performed using the GAUSSIAN94 program package [17].

We have made first-principles calculations of the Fermi contact constants for both the Cl and D nuclei as a function of the bond length for DCl^{2+}, and we have found that there is only a weak dependence on vibrational state (2% difference between $v=2$ and $v=1$). We have therefore ignored this vibrational dependence in our preliminary determination of the experimental hyperfine constants. Our calculated value of the deuterium Fermi contact interaction in DCl^{2+} is -16 MHz, which is similar to the deuterium Fermi contact interaction of -7 MHZ measured in the isoelectronic species PD [18]. We were therefore confident that our theoretical value for the chlorine Fermi contact interaction ($\approx$190 MHz) would be close to the experimentally determined value.

The Hamiltonian for fine structure contains a spin-splitting term λ that is due to a direct contribution from the spin-spin interaction (λ^{SS}) and a second-order (and usually dominant) contribution (λ^{SO}) from spin-orbit interactions with other electronic states. We estimate λ^{SO} from the isoelectronic spectra of SH^+ [19], where $\lambda=5.7$ cm^{-1} (171 GHz), by suitable scaling using the square of the ratio of atomic spin-orbit parameters for S^+ and Cl^+ and the energy separations between the $^3\Sigma^-$ and $^1\Sigma$ states in each case [20]. We arrive at an estimated value of $\lambda=11.5$ cm^{-1} (345 GHz). We estimate the value of γ, the spin rotation constant, to be -0.1 cm^{-1} (-300 MHz) from values of isoelectronic species. The rotational constants were calculated from first principles [8], and we note that in both $v=1$ and $v=2$, $B\approx3.4$ cm^{-1} (102 GHz). In DCl^{2+}, using these constants ''pure'' case *b* behavior is reached by $N=15$, but even for $N=0$ there is at most a 25% mixing with nearby rotational levels.

We have not yet reached an unambiguous rotational assignment of the observed lines in the infrared spectrum of DCl^{2+} because of the partial frequency coverage of our experiment. However, in order to make a preliminary analysis of the hyperfine structure that we have observed, we may make a simplifying assumption. The rotational levels are separated by ≈7 cm^{-1} (210 GHz) and the fine-structure components by ~11 cm^{-1} (330 GHz); these are large compared to the hyperfine splittings of approximately 7×10^{-3} cm^{-1} (200 MHz). Consequently, the hyperfine interaction can be treated as a small perturbation of the widely spaced terms. We calculate the matrix elements of the hyperfine interaction in a case (b) basis. Elements off-diagonal in N and J are sufficiently small that they can be ignored.

Experiment. A description of our experiment has recently appeared [8], as has a general discussion of ion-beam spectroscopy [21] both of which may be consulted for details regarding techniques. The ion of interest is selected by its mass/charge ratio by means of a magnetic sector and subsequently illuminated by radiation from a line-tuneable CO_2 laser (Edinburgh Instruments PL3). Frequency scanning is achieved through the Doppler effect by using a small scanning voltage on a Faraday cage. We detect transitions indirectly by monitoring the fragment ion (usually Cl^+) current that changes at resonance. The fragment ions are selected using a cylindrical-plate electrostatic analyzer and monitored using an off-axis electron multiplier. Signals are detected with a lock-in amplifier (SR 850; laser chopper SR 540). We have no means of measuring absolute transition strengths, but we assume that the noise level is constant throughout the spectrum and use (signal/noise)/(laser power) as a relative measure of line intensity. Our ability to resolve the hyperfine structure is due to the kinematic compression of the Doppler width, which gives sub-Doppler resolution [21]. Our limiting instrumental linewidth is approximately 24 MHz for the spectrum shown.

Our electrostatic analyzer does not have sufficient resolution to measure the beam energy to better accuracy than our systematic uncertainty. We pessimistically estimate that at a beam potential of 5000 V, the uncertainties in our absolute transition wave numbers are presently on the order of 0.002 cm^{-1} (60 MHz). However, where multiple lines are observed in a single scan (as in Fig. 2), reproducibility is excellent, and the predominant uncertainty in the relative wave numbers (separations) between lines is determined only by the accuracy with which the line centers can be measured by fitting a suitable line shape function i.e., to about 5 MHz.

Our initial measurements [8] showed that we are almost certainly examining *P* and *R* branch transitions of the $v=2$-1 band of DCl^{2+}. We reached this assignment by comparing theoretical spectra [22] with the strongest lines that we observe. The theoretical spectra were generated from a first-principles calculation using the potential-energy curve of Bennett and McNab [22], which has also been found to yield theoretical spectra in excellent agreement with a vibrationally resolved threshold photoelectrons in coincidence (TPeSCO) spectrum of HCl^{2+} [23].

Besides the strong lines that we have observed, we have also detected some of the much weaker $^PQ(N)$- and $^RQ(N)$-branch satellites to the main triplets (see Ref. [24] for notation). These satellite lines display a characteristic quartet structure that is caused by the nuclear spin of the chlorine nucleus ($I=\frac{3}{2}$). There is also a characteristic intensity alteration due to the degeneracies of the initial and final states; across each quarter the total angular momentum of the states involved in the transition changes from F to $F\pm3$.

Analysis. We show a diagram of the relevant energy levels and allowed transition in Fig. 2. For the particular case of these $^PQ(N)$- and $^RQ(N)$-branch transitions, relative intensities within a particular quartet spectrum are given by the expression

$$I_{\mathrm{rel}}\propto(2F'+1)(2F''+1)\begin{Bmatrix}3/2 & J & F'\\ 1 & F'' & J\end{Bmatrix}^2,$$

where J equals $N+1$, N, or $N-1$ depending upon the particular $^PQ(N)$ or $^RQ(N)$ transition. The $\Delta F=0$ transitions are the strongest and account for the four main lines whose intensity varies as $(2F+1)^2$.

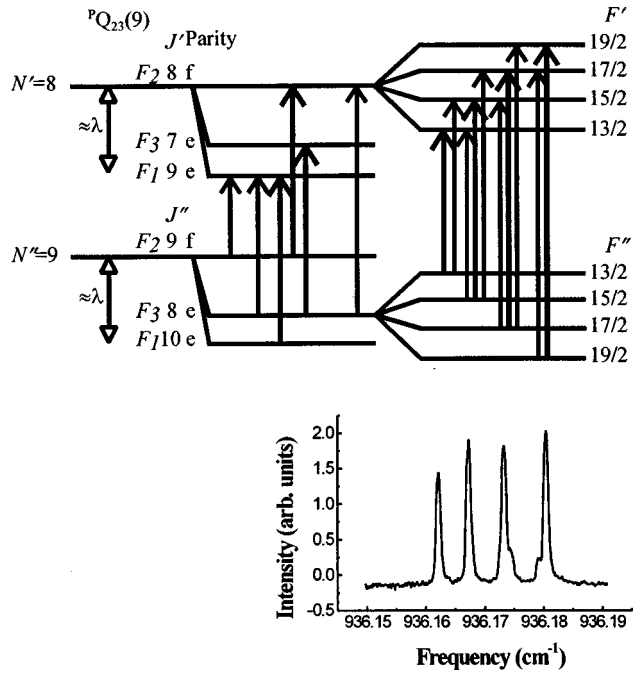

FIG. 2. A hyperfine resolved infrared transition, $^{P}Q(9)$, in the $v=2\leftarrow1$ band of $D^{35}Cl^{2+}$ with center wave number of 936.171(3) cm^{-1}. The energy-level structure of the contributing levels are shown above, and the transition wave numbers are given in Table I. The spin-splitting constant, $\lambda\approx11.5$ cm^{-1}, is dominated by a second-order-spin-orbit contribution, λ^{SO}. The recording of the transition shown was saturated using high laser powers to allow observation of weak lines and the relative intensities are not representative of intrinsic transition probabilities. The well-resolved hyperfine structure in this transition is seen to be a consequence of the different parity of the levels involved, which inverts the terms for the same F values.

A hyperfine-resolved transition is shown in Fig. 2. We determined the F values of the lines by assuming Lorentzian line shapes for the four main transitions and using a least-squares fit to determine the relative intensities, the best fit gave $N''=9$. The spectrum used in this assignment was not the one shown, but was taken at the lowest possible laser power in order to avoid saturation of the lines. The two weakest lines in the spectrum (clearly visible in Fig. 2 as shoulders on the highest wave-number intense lines) were not visible in the spectrum used for assigning the F quantum numbers. We believe that this method of assigning the F quantum numbers gives an uncertainty of $N\pm2$.

The center frequency of the quartet is 936.171(3) cm^{-1}, and from our previous analysis we know that this quartet belongs to the P branch of the spectrum. This being so, we arrive at the preliminary assignment $^{P}Q_{23}(9)$.

In order to determine the hyperfine splittings as accurately as possible, we used a least-squares fit to the spectrum shown in Fig. 2, which was taken at high laser power, in order to take advantage of the positional information from the weaker lines. Six transitions are clearly visible. We found the line positions using a Lorentizan peak shape for each peak. The line positions and assignments are given in Table I.

TABLE I. Measured transition wave numbers and assignments based on a fit to relative intensities; the absolute transition wave numbers are reproducible to 0.003 cm^{-1} (90 MHz), but separations are reproducible to 0.001 cm^{-1} (3 MHz).

Transition wave number (cm^{-1})	Label	Assignment (F', F'')	Separation from a in MHZ
936.161 88	a	13/2, 13/2	000.0
936.166 68	b	15/2, 15/2	144.0
936.172 74	c	17/2, 17/2	325.8
936.173 65	d	19/2, 17/2	353.1
936.178 39	e	17/2, 19/2	495.3
936.179 78	f	19/2, 19/2	537.0

We calculated hyperfine matrix elements in Hund's case ($b_{\beta J}$) that were in agreement with the matrix elements for $^{3}\Sigma$ states previously published by Frosch and Foley [10] (magnetic hyperfine interaction only) and also by Ubachs *et al.* [25] (magnetic and electric quadrupole hyperfine interactions).

If pure case (b) behavior is assumed, the expressions are linear in the constants to be determined, and so we used our line separations together with the theoretical expressions for the matrix elements to determine the hyperfine constants directly in a linear least-squares fit, assuming pure case (b) behavior.

From our linear least-squares fit we determined values for the Fermi contact constant, b_F, but the magnitude of the uncertainty in the determination of the axial dipole–dipole interaction was greater than its value, and hence it remains undetermined. Attempts to include the electric quadrupole interaction into the fit led to physically unrealistic magnitudes for the constants.

The assignment of $N''=9$ may be subject to an uncertainty of ±2, and so we report the results of fits for $N''=7-11$ in Table II. Our previous assignment of the observed strong lines in the spectrum favors the assignment $N''=7$. In order to take account of the omission of state mixing that we have made by using pure case (b) matrix elements in our linear least-squares fit, we have also used a complete diagonalization of the Hamiltonian made using the program PGOPHER [26] to adjust the least-squares values; the result of a full diagonalization is that slightly lower separations are produced for a given set of hyperfine constants. The limiting separation of the hyperfine-resolved transitions at high N is determined by $b+c=b_F+\frac{2}{3}c=A_{\|}$, which is the axial component of the magnetic hyperfine interaction [27], and so we have simply scaled the linear least-squares values by the ratio of predicted separations in the hyperfine pattern in the single state, pure case (b), and fully diagonalized calculations to arrive at our final (scaled) values for the constants and their uncertainties. As would be expected, the well-determined Fermi contact constant, b_F, has essentially the same value regardless of J assignment: 167(25) MHz. The positive sign of the Fermi contact constant is supported by both our calculations and by the fact that the sign of the Fermi contact constant in the isoelectronic molecule PD is

TABLE II. The assignment of $N''=9$ may be subject to an uncertainty of ± 2, and so we report the results of linear least-squares fits for $N''=7$–11. Values are given as best value (one standard deviation in units of last figure).

	Hyperfine constants (MHz)						Center wave number[a] (cm^{-1})
	Fermi contact constant (b_F)				Dipole-dipole constant (c)		ν_0
	Experiment		Theory		Experiment		
Assignment	LSF[b]	Scaled LSF	$v=1$	$v=2$	LSF[b]	Scaled LSF	
$^PQ_{23}(7)$	181 (18)	166 (16)	192.8	189.6	51 (60)	47 (55)	936.1710 (1)
$^PQ_{23}(8)$	188 (23)	167 (20)	192.7	189.5	69 (77)	61 (68)	936.1710 (1)
$^PQ_{23}(9)$	194 (28)	167 (24)	192.6	189.3	87 (94)	75 (80)	936.1709 (2)
$^PQ_{23}(10)$	210 (34)	167 (27)	192.5	189.3	105 (111)	84 (88)	936.1708 (2)
$^PQ_{23}(11)$	207 (39)	168 (36)	192.4	189.1	124 (128)	100 (104)	936.1708 (2)

[a]Systematic uncertainty≈ 0.003 cm^{-1}. [b]LSF-linear least-squares fit.

also positive for the phosphorus nucleus [18].

The determination of all the hyperfine constants to a good accuracy for the interactions between the electronic structure and the chlorine nucleus should be possible from a full analysis of all the spectra that we have obtained, but this must wait upon a complete assignment.

Conclusion. We have measured a hyperfine-resolved infrared spectrum of DCl^{2+}. A preliminary analysis shows that the Fermi contact (isotropic-hyperfine) coupling constant in the $v=2$ and 1 vibrational levels is 167(25) MHz, in good agreement with our first-principles calculations. Experiments are currently in progress to examine the hyperfine structure under still higher resolution in a radio-frequency/infrared double-resonance experiment, and to examine Zeeman splittings to arrive at unambiguous assignments of F quantum numbers. If our experiments are successful, we will be able to arrive at a final assignment of the complete spectrum and determine the extent of electron sharing between the chlorine and deuterium nuclei in the molecular dication DCl^{2+}.

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